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(Continued from page 3 of cover.)

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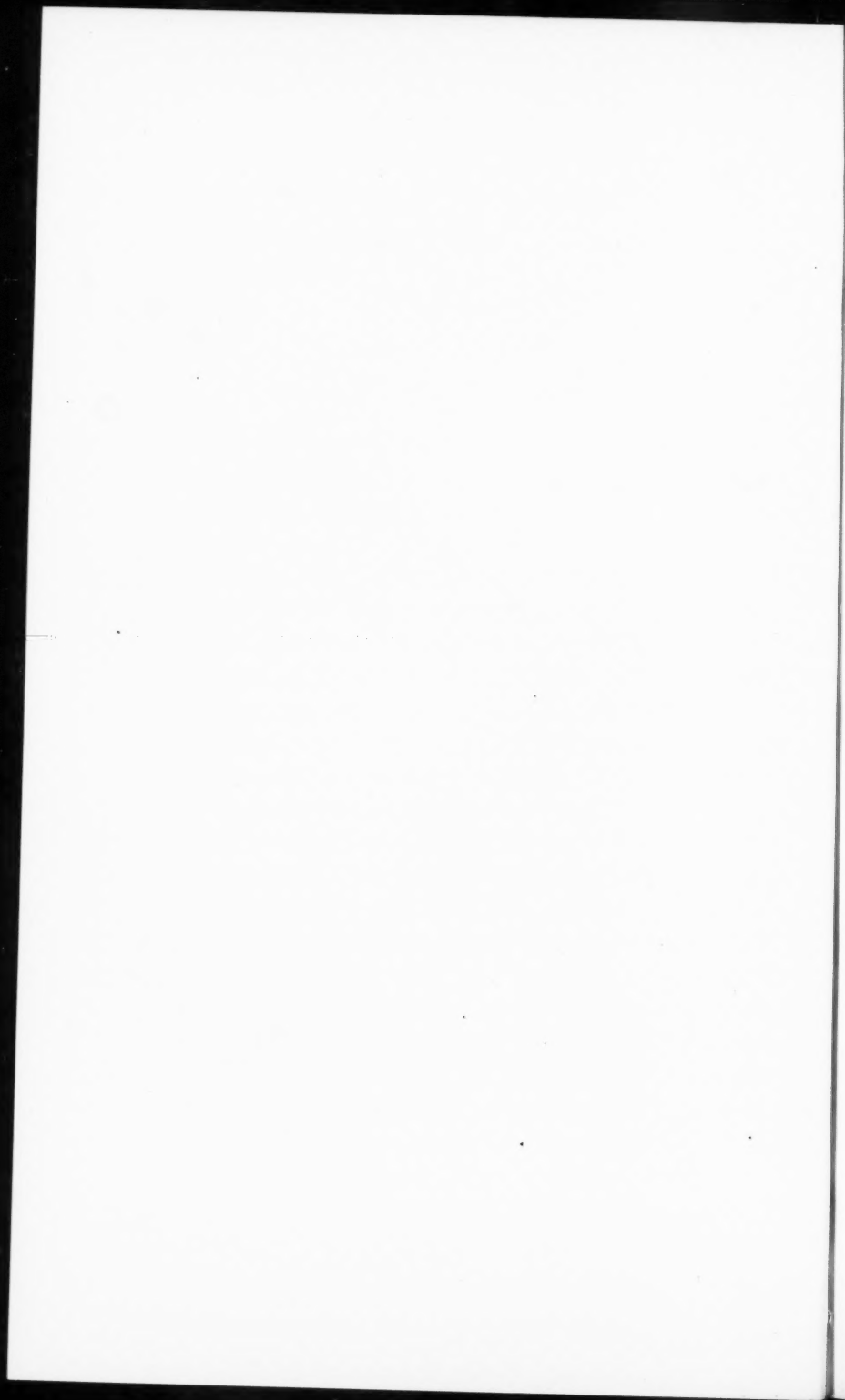
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INTRODUCTION.

DURING the last few years a revival of interest in the question of the possible existence of a critical point between solid and amorphous phases has been inspired by new measurements on several of the permanent gases, a particularly simple class of substance. These measurements are due primarily to Simon and his collaborators,¹ who have followed the melting curve of helium to approximately 5500 kg/cm², that of hydrogen to 5000, that of neon to 4900, that of nitrogen to 5000, and that of argon to 3400. However, there are also a number of measurements from the laboratory at Leiden,² over a much smaller pressure range, but with greater precision. It is the opinion of Simon that the melting curve will end in a critical point, but in no case has such a critical point actually been realized. In the failure actually to realize the critical point the course of the melting curve itself can give no basis for an extrapolation, which can be made only with the help of other independent data. Thermodynamically, the critical point is characterized by the simultaneous vanishing of the difference of volume between the two phases and of the latent heat of the transition. If a critical point is to be justifiably inferred from extrapolation from data in the experimental region, then the course of the curves for difference of volume and latent heat in the experimental range must be such as to indicate the vanishing of the volume difference and the latent heat within distances not too remote from the region of experi-

ment, and furthermore, the extrapolated vanishing pressure (or temperature) for volume change must be the same as the extrapolated vanishing pressure (or temperature) for latent heat. Simon did not make measurements of either change of volume or of latent heat, so that up to the present there is no basis for extrapolation, and no possibility of setting up a rigorous argument for a critical point, from the new data for the permanent gases.

In this paper I present new measurements of the coordinates (pressure and temperature) of the melting curves of argon and nitrogen up to about 5500 kg/cm², and also measurements of the difference of volume. As is well known, the latent heat of the transition may be computed from the volume difference and the coordinates of the melting curve by means of Clapeyron's equation, so that we now have the means of making an extrapolation toward a possible critical point for these two gases. Furthermore, in the course of the measurements of the volume difference it was necessary to know the volumes of the gaseous phase; these apparently have not been previously determined at temperatures below 0° C at pressures higher than 200 or 300 kg, so that it was necessary to determine a number of points on the p - v - t surface of the gas in the new region. These determinations, which have an interest in themselves apart from the problem of change of phase, are also given in the following.

APPARATUS.

The large features of the apparatus were determined by the general method, which was the same as that employed in my previous work on change of phase of substances liquid under ordinary conditions.³ Pressure was produced by the motion of a leak-proof piston. Change of phase is accompanied by a discontinuity in the motion of the piston as a function of pressure. The pressure of the discontinuity at a given temperature gives the p - t coordinate of a point on the melting curve, and the amount of discontinuity gives the volume change. These new measurements differ from the previous ones in that gases are being dealt with instead of liquids, and by the low temperatures, running down to 77° K, so that appropriate changes in the apparatus were necessary.

The apparatus already employed for the measurement of electrical resistance as a function of pressure at low temperatures⁴ could be adapted to the demands of this method with very few changes. The apparatus consists essentially of a couple of precompressors, by which

the gas is raised from the tank pressure of approximately 100 kg/cm^2 to 2000 kg/cm^2 , an upper cylinder maintained at room temperature, in which pressure is produced by the motion of a leak-proof piston, and in which is installed the manganin gauge by which pressure is measured, a connecting pipe, and the lower cylinder, maintained at the desired temperature by a low temperature thermostat to be described later, in which the freezing of the gas takes place. The diameter of the hole in the upper cylinder was about 0.67 cm , and its length 8.6 cm , making a total capacity in the upper cylinder of about 2.8 cm^3 . The lower cylinder was also 0.67 cm in internal diameter, with a total capacity of about 3.8 cm^3 . The connecting pipe was 30 cm long, with a total internal volume of 0.13 cm^3 , and an outside diameter of 0.48 cm . The upper cylinder carries only one side hole, that for the manganin gauge, instead of the four holes which were necessary in the previous experiment; this results in a very desirable simplification of construction and assembly. The screw plug by which the manganin gauge is retained against pressure is carried in a heavy ring, girdling the cylinder, and a push fit for it, as in the previous experiments.

In my previous measurements of change of phase under pressure, the substance undergoing transition was usually separated from the pressure transmitting liquid, which was some light hydrocarbon, by mercury. This is now obviously impossible; furthermore, there seems to be no method of separating one fluid from another without mixing in the range of pressures and temperatures involved, so that the entire apparatus had to be filled with the substance whose transition was being measured. This necessity gave rise to considerable misgiving, for I had already tried without success to measure the compressibility of some of the permanent gases by the piston displacement method. The difficulty was the penetration of the steel by the gas, having the same effect, as far as measurements of volume in terms of piston displacement are concerned, as a leak. It was the same penetration of the steel by the helium which set the maximum limit of 7500 kg/cm^2 reached in my previous experiments on resistance at low temperatures. However, previous experiments had shown that penetration by nitrogen is usually not nearly so serious as penetration by helium, and on one occasion I had reached a maximum pressure of 12000 kg/cm^2 with nitrogen, although this could not be permanently retained, so that the problem did not appear hopeless if one were willing to restrict oneself to comparatively low pressures. It appeared,

moreover, that Simon had been having no such difficulty as I from the penetration of his steel. I therefore obtained, through the kind offices of Dr. Simon, for which I am very much indebted to him, from the German firm Bismarckhütte, Berlin, some of the same steel which he had been using. A test cylinder made from this withstood without rupture a maximum pressure of 12000 kg/cm^2 exerted by helium, although the pressure was not permanently retained, but slowly dropped, thus showing some absorption by the steel. The performance was very much better than that of any steel which I had previously tried, however, and the entire apparatus was therefore constructed from this German steel. It is a chrome-nickel steel, the exact composition of which I do not know, but it is obviously low in carbon. It is supplied in a heat treated condition, soft enough for ordinary machining operations, with a tensile strength of about $150,000 \text{ lb/in}^2$. The upper and lower cylinders were machined from the steel as supplied. The steel was too hard, however, to permit drilling the hole 30 cm long and 0.08 cm in diameter for the connecting pipe, so that the steel from which the pipe was made was first annealed and then reheat-treated after fabrication.

The apparatus constructed from this steel was used in obtaining the results described in the following up to a maximum pressure of about 6000 kg/cm^2 with no sign at all of penetration either by nitrogen or argon. One connecting pipe split during use, but the original upper and lower cylinder were used throughout. I have not yet had enough experience in handling gases at high pressures to know whether the superior performance of this steel is due to its chemical composition, or to its superior homogeneity and freedom from various sorts of imperfections. This sort of steel is, of course, made in this country also, but I have not yet tried any of American manufacture. One or two metallurgists have suggested that the German steel may be intrinsically superior for this sort of service because it is much freer from impurities of sulfur and phosphorus, the original Swedish ore from which German steels are made being known to be freer from sulfur and phosphorus than any American ores. Sulfur and phosphorus are said to be the most likely constituent of impurities which tend to segregate mechanically in the ingot, which one would expect to result in gas penetrability. If it should turn out that the employment of a CrNi steel, like that used here, is necessary in high pressure gas work, the pressures attainable with gases in experiments of this character would be definitely limited to about 12000 kg/cm^2 , the

stretch beyond this point in a steel not capable of being heat treated to higher figures becoming too great to permit accurate measurements of volume by the piston displacement method. However, up to pressures of this order it would seem that it is now possible to explore the p - v - t surface of gases by a technique distinctly simpler than that used in my previous work. It appears, furthermore, that there are several new possibilities which I have not yet explored in the way of homogenizing steels during the process of manufacture, so that it is not at all impossible that pressures still higher than this will presently be available for experiments of this character on gases.

The motion of the piston which gives the change of volume was measured in two different ways. The first method was that already employed in measuring the compressibility of gases. The hardened plunger is pierced with a small axial hole, through which passes a wire made an integral part of the head of the moving packing plug. The position of the upper end of this wire is read through a suitable peephole milled in the piston of the hydraulic press with a reading telescope and a scale attached to the upper cylinder. In this way the actual motion of the moving plug in contact with the gas is measured, and errors from compression or wear of the packing are eliminated. The second method measures the motion of the piston of the hydraulic press with respect to the upper cylinder by means of two Ames dial gauges of one inch stroke, graduated to 0.0005 inch and easily read to 0.0001, mounted on opposite sides of the press. Calibrated extension rods were provided by which the range could be extended as required beyond the one inch capacity of the gauges. This scheme is much like that used by Adams at the Geophysical Laboratory in his measurements of various compressibilities by the piston displacement method, except that two gauges are used instead of one, thus making possible the more complete elimination of the effects of distortion in the press. The two gauges usually agreed to about 0.002 inch over the entire stroke. The gauges were calibrated over their entire stroke with gauge blocks, and the maximum error found was 0.0005 inch, although the error in a couple of gauges which were discarded was more than this. The mean of the readings of the two gauges should be free from the effects of distortion or other error within about the sensitiveness of the readings. The second method is very much more convenient than the other because the Ames dials are much easier to read than the telescope. After one or two runs had disclosed no perceptible difference between the piston displacements given by

the two methods, showing no perceptible wear in the packing, the Ames gauges only were used after the initial measurement, when the telescope and scale also was used in order to give the absolute position of the plunger and so a fiducial point from which could be calculated the absolute volumes which enter into some of the corrections. It proved on working up the results, however, that variations in the initial volumes affect the corrections only within wide limits, so that the information given by the absolute position of the piston did not prove to be important.

The upper cylinder was not provided with a thermostat, but was at room temperature. A small oil bath was built around the cylinder above the ring carrying the screw plug of the manganin gauge, and the temperature was read a number of times during a run with a thermometer immersed in this oil bath. The variation of temperature during a run was seldom more than a few tenths of a degree, and the corrections for this small variation were so easy to apply that the complication of a thermostat was not justified.

The manganin gauge was the identical one which had been used in the previous work on resistance at low temperature; it was wound from wire 0.003 inch in diameter, obtained from Driver Harris. It was however, now subjected to a fresh seasoning procedure, the zero drift having become, in the two years since previously used, somewhat larger than desirable. The seasoning consisted in maintaining it continuously at a temperature of 135°C for three days, except for two excursions for five minutes each to the temperature of solid CO_2 . The resistance was lowered 0.45% by the seasoning, and the pressure coefficient dropped 1.79%. The pressure calibration was made in the usual way in terms of the freezing pressure of mercury at 0°C . The drift of the zero was very much reduced by the new method of seasoning; the change of zero in three months time now amounting to an increase of 0.005% of the total resistance. Because of the necessity of getting closely spaced pressure readings in the neighborhood of the transition points, the sensitiveness of the pressure readings was increased nearly five times beyond that of the previous work by increasing the size of the slide wire of the bridge. With the new arrangements, 1000 kg/cm^2 corresponds to a slider displacement of about 24 cm, and it was possible to get readings consistent to 0.1 mm, or about a quarter of an atmosphere, over the entire pressure range. The absolute accuracy of the calibration, of course, does not correspond to this sensitiveness, but small differential effects could be obtained corresponding to this sensitiveness.

The lower cylinder, in which freezing takes place, has to be maintained at constant temperature at any desired point in the range from 77° K to 185° K, and this demanded the construction of a special thermostat. In the previous work only the temperature of boiling oxygen was used, so that formerly the problem was very simple. Boiling oxygen was also used as one of the fixed temperatures in this work, and to this was added boiling nitrogen. The liquid nitrogen was obtained by passing nitrogen from a tank of commercial nitrogen, "99.7% pure," through a copper coil immersed in liquid air, there being a throttle valve on the outlet end so as to maintain a pressure of at least five atmospheres in the gaseous nitrogen and thus permit its liquefaction at the temperature of liquid air. Corrections were made for the barometer when using either of these boiling baths, as had also been done in the previous work.

Above the temperature of boiling oxygen there are no available substances boiling within the range desired, and some sort of stirred and thermostated bath seemed the only possibility in view of the necessity of raising and lowering the cylinder into the bath in order to control the freezing, as will be explained later. The problem of a stirred bath in this range of temperature is one which has been encountered by many other experimenters and has never proved easy of solution. The conditions were in this case perhaps more exacting than usual because of the unavoidably large heat leak into the bath along the connecting pipe. I made a number of attempts before finding the solution adapted to the needs of this particular experiment. The bath liquid finally used was liquid propane, obtained by passing the gas, sold commercially under various trade names in compressed cylinders for domestic use in places where there is no municipal gas supply, through a copper coil immersed in CO_2 and alcohol. The liquefied propane is contained in a thin German silver can of about one half liter capacity, surrounded for heat insulation by a special thermos flask pierced with a hole through the bottom. The propane is stirred by a small turbine stirrer of conventional design. Passing through the propane bath are several turns of light walled copper tubing, connected at the upper end with a source of vacuum, and at the bottom end, through the bottom of the pierced thermos flask, with a source of liquid air. When the temperature rises too high, liquid air is automatically sucked up into the copper tubes, lowering the temperature of the surrounding bath, until the vacuum is again cut off. The temperature regulating member is essentially a hydro-

gen pressure thermometer. A thin walled copper bulb, of about 8 cm³ capacity, connects through hypodermic steel tubing of 0.02 cm diameter with a mercury column provided with suitable contacts. The bulb also connects, through suitable reducing valves, with a tank of commercial hydrogen. The height of the mercury column is so chosen that the hydrogen in the bulb is under a pressure of about two atmospheres, thus increasing the sensitiveness. The contacts are made through a vacuum tube arrangement through a thyatron, so that the motor which runs the vacuum pump can be turned on and off with no sparking at the contacts; the sensitiveness is so great that the contact makes or breaks with no motion of the mercury column perceptible to the eye. The bulb was always carefully filled with hydrogen by flushing from the tank a number of times to remove the atmospheric air. It was found that use of hydrogen instead of air greatly improves the performance, both because of the better heat conductivity of the hydrogen, and because of the diminished resistance in the connecting capillary. Sluggishness of response due to viscous resistance in the capillary limits the sensitiveness of this device; if the size of the capillary is increased too much, error is introduced by fluctuations in room temperature because of changes in the volume of that part of the gas exposed to the temperature of the room.

In order to avoid danger from ignition of the propane vapors which might escape from the bath into the room, a small ventilating hood was built around the lower end of the press and connected with a ventilating fan. Evaporation was prevented as much as possible by the use of a fairly tight fitting cover over the propane bath, but this had to be removed during the manipulations incidental to freezing, so that during a run of several hours perhaps as much as 50 cm³ of propane was lost by evaporation. This was replaced several times during the run from a special source of supply, so that the level of the bath was maintained approximately constant, an important point in order to avoid errors in the volume due to fluctuations in the temperature of the pipe. One anticipated source of danger was the explosion which might result from a mixing of propane with the liquid air if there was a rupture of the lower cylinder. Fortunately the lower cylinder remained intact during all the runs, but this source of danger was in any event minimized by surrounding the thermos flasks containing both propane and liquid air with heavy steel walls so that, if rupture of the lower cylinder did take place, only the small amount

of liquid air which might happen to be in the cooling spiral would come in contact with the propane.

Before using propane I tried some of the non-inflammable liquids recommended for cryostats by the Bureau of Standards, which are described in International Critical Tables, vol. I, p. 61. It proved that although these might be practicable at the upper end of the temperature range as far as their behavior at that temperature only is concerned, they at once become of the viscosity of vaseline on the wall of the cooling spiral when the liquid air is sucked into the spiral, and for this reason were totally unfit for use in my particular form of cryostat.

Temperature was measured with a copper-constantan thermocouple, using a standard cell and Leeds and Northrup potentiometer, Type K, for the measurements of voltage. One junction was maintained at 0°C in a thermos flask filled with ice, and the other junction was immersed directly in the propane of the bath at a point very close to the wall of the pressure cylinder. The sensitiveness of the potentiometer corresponded to about 0.03° . The thermocouple was calibrated at the boiling points of nitrogen and oxygen and at the subliming point of solid CO_2 . The voltages at these temperatures were compared with those given by Adams for a copper-constantan couple in International Critical Tables, I, 57, and a smooth deviation curve was drawn through the points representing the difference of the readings. The temperatures corresponding to other voltages were obtained by a combination of Adams's tables with the deviation curve. The error in such a procedure should not be more than 0.05° at any point, which was sufficient for the purposes in hand. A second copper-constantan couple, connected to a sensitive millivoltmeter, served as a thermometer in giving a constantly visible indication of the temperature, but not with the accuracy of the potentiometer readings.

The bath temperature, except of course when boiling oxygen or nitrogen was used, fluctuated back and forth through an extreme range of 0.5°C with a period of about two minutes. The extreme temperatures were read several times during the course of a run and the mean taken as the true temperature. At the interior of the pressure cylinder the temperature fluctuations of the bath were to a large extent wiped out, but nevertheless, sometimes when both liquid and solid phases were present together, the temperature fluctuations were manifest in a small oscillation of pressure lagging almost 180° behind

the temperature fluctuations of the bath. Under these conditions the mean temperature was taken as corresponding to the mean pressure. When only one phase was present the pressure fluctuations were too small to be perceptible.

In addition to the measurements with the apparatus just described of the coordinates of the melting curve and the changes of volume, it was necessary also to know the specific volume of the gaseous phase in the range of pressure and temperature involved. The reason for this is that the measured discontinuity in the motion of the piston gives the change of volume on freezing of that quantity of the solid which occupies a known volume, that is, the volume of the lower cylinder, under the given conditions, whereas what is thermodynamically significant is the change of volume per gram. A knowledge of a specific volume is therefore necessary. It has already been stated that no specific volumes are known in the range of pressures and temperatures involved here. However, it is very easy with this apparatus to make connection at any pressure between the volume at any temperature in the range below 0°C , and at temperatures in the range above 0° , merely by changing the temperature of the lower cylinder from the one value to the other and observing the amount by which the piston must be withdrawn to maintain pressure constant. Hence if the specific volumes are known over the requisite pressure range at some temperature above 0°C , the present apparatus readily supplies the additional information necessary. Now the specific volumes of nitrogen are known above 0°C , from the work of Amagat up to 3000 kg/cm^2 , and from my own previous work above 3000 . No such information exists for argon, however; it is true that I have measured the *changes* of volume above 2500 kg , but these results cannot be converted into specific volumes until the volume is known at some one fiducial point in the range. To obtain the one fiducial point another simple piece of apparatus was necessary. This consisted merely of a small steel bottle of known volume which could be filled with argon to a known pressure and sealed off from the source of supply. The total weight of the bottle filled with gas was then measured, and again after the gas had been allowed to escape. The bottle was made of a stainless steel sold under the trade name of "Alleghany 44." It is shown in Figure 1. The closure by the piece B was copper welded into place in an atmosphere of hydrogen, and was thus gas-tight. The capacity to the point C was then determined by weighing empty and filled with air-free distilled water. The interior

volume was 1.26 cm^3 . A steel capillary of 0.008 inch internal diameter and 0.120 inch external diameter was then soft soldered into the piece B, the threads being first tinned carefully both inside and out,

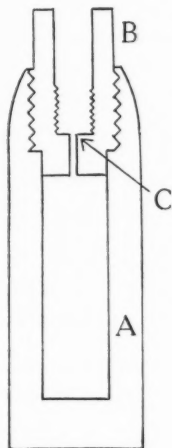


FIGURE 1. The steel bottle for obtaining a fiducial point on the $p-v-t$ surface.

and there being also an arrangement of steel retaining rings, not shown in the diagram, to prevent the extrusion of the soft solder by pressure. The other end of the steel capillary was connected to the high pressure apparatus by soft soldering into a cylinder shown in Figure 2, which replaces the lower cylinder of the freezing apparatus. The crux of the situation is the piece of Wood's metal A, contained in the connecting cylinder. In use, the bottle was maintained at 0°C and filled with argon to a measured pressure. The connecting cylinder and the upper 10 cm of the steel capillary were then raised to the boiling point of water, melting the Wood's metal A. An excess pressure of 500 or 1000 kg/cm^2 now forced melted Wood's metal into the capillary until it reached the cold part, where it froze. The connecting cylinder was now chilled, and the capillary cut off where it joins the cylinder, thus giving the bottle with gas sealed into it at known pressure. Weighing to the requisite accuracy was easily done

by attaching to the under side of the scale pan of a balance through a hole cut in the case. The actual filling was made at a pressure of

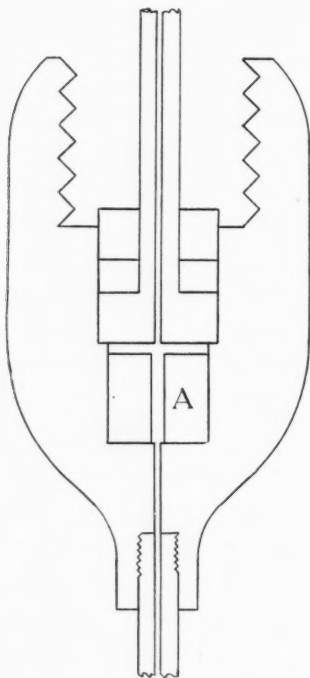


FIGURE 2. Shows the connecting piece through which the bottle of Figure 1 is filled. The piece of Wood's metal A is melted after filling, thus sealing the gas into the bottle.

1070 kg/cm², and the weight of the gas was 1.030 gm. An attempt to get a second fiducial point from a filling at 1500 kg/cm² was unsuccessful because of leak around the soldered joint of the steel capillary. The interior of the steel capillary was found to be far from smooth; in places the cross section was roughly star shaped with sharp corners. This means that the absolutely tight sealing of the capillary with

melted Wood's metal was not the perfectly simple thing that would be suggested by the description above, but additional manipulation was necessary, pinching the capillary nearly flat in places with a heavy clamp, and remelting and resolidifying several times the Wood's metal between the pinched places. A perfectly tight seal can at once be tested by immersing the cut end of the capillary in water, and it was only after a number of attempts that such a perfectly tight seal was obtained.

There are a couple of small corrections to be applied; one for the thermal expansion of the steel of the bottle, for which the figure of the manufacturers (0.0000162 mean linear expansion between 20° and 100° C) was assumed, and a very small correction for the capacity of the capillary. The correction for the distortion of the bottle under internal pressure is too small to be appreciable.

The measurements with the bottle just described give a fiducial point at 1070 kg/cm², and the lowest pressure of my previous measurements was 2500. The interval between these two sets of measurements was spanned by making two sets of isotherms at room temperature, one with the same lower cylinder as that used in the melting measurements, and another with the same lower cylinder nearly filled with a known amount of steel. The difference of the piston displacements of the two isotherms gives the volume compression of the amount of gas occupying the volume of the steel, the various unknown factors, such as the effect due to the compression of the packings, dropping out when the difference is taken. By this means the new point at 1070 kg/cm² was connected with the previous work at 2500 and higher.

EXPERIMENTAL PROCEDURE.

The experimental procedure consisted mostly of perfectly straightforward adaptations and modifications of procedure used in previous measurements of phase change or of compressibility by the piston displacement method and need not be described in detail except for a few special points. The initial filling of the apparatus must be done in such a way as to get rid of most of the atmospheric air originally present, which otherwise will act as a dissolved impurity, depressing the freezing point and rounding the corners of the transition curve so as to obscure the true change of volume. In the case of nitrogen, of which a plentiful supply was available, this was accomplished by flushing out the apparatus three times from the original supply.

Since the pressure in the supply tank is of the order of 100 atmospheres, the original impurity is reduced by three flushings to 10^{-8} of the total, a wholly negligible amount. In the case of argon (because of its greater value), this procedure was modified by initially exhausting the apparatus to about 1/100 atmosphere, filling once with argon at 100 atmospheres, exhausting again to 1/100 and finally filling again with argon to 100, thus again reducing the proportion of atmospheric impurity to 10^{-8} .

The approximate location of the freezing curve was already known from the work of Simon. The freezing point was of course approached from the gas side, plotting the readings of piston displacement against pressure as each point was obtained. In this way the first beginning of freezing was at once caught. Special manipulation was now necessary in order to fill the lower cylinder with the solid phase and prevent freezing in the connecting pipe, which would have led to an incorrect and too small value for the change of volume. This was accomplished by lowering the bath from around the lower cylinder until only the lower part of the cylinder was dipping in the bath liquid, and then pushing the piston in by a number of small steps, perhaps 10 or 12 altogether, and at the same time raising the bath back until the cylinder was again completely immersed and also the connecting pipe up to the former mark. In this way the lower cylinder was forced to freeze solidly full from the bottom up. After complete freezing had been accomplished, pressure was raised about 200 kg beyond the freezing point. Care must be taken not to push pressure too far beyond the freezing point or else the plug of solid in the pipe will yield, transmitting pressure to the solid in the cylinder, so that the change of volume measured will be that between the gas at the transition pressure and the solid at a somewhat higher pressure, which would give too large a change of volume. Readings were now made with decreasing pressure, perhaps at 40 kg intervals above the freezing point, several in the two phase region with varying proportions of the two phases, and then several in the gaseous phase, locating the first reading in the gaseous phase as close as possible, usually within 40 kg, of the lower corner of the discontinuity, so as to minimize error by making only a short extrapolation necessary. It is obvious that having once filled the lower cylinder full with the solid phase, no such precautions were necessary in lowering pressure as in raising it, and these readings could be made rapidly. The small size of the apparatus and increased thermal conductivity at low temperatures much facil-

itates the procedure compared with previous transition measurements at higher temperature, and the whole series of readings with decreasing pressure could be made in less than an hour. Both the pressure-temperature coordinates of the melting curve and the change of volume were taken from the readings with decreasing pressure, these being more reliable than the readings with increasing pressure.

The discontinuity in piston displacement given directly by the readings does not yield at once the change of volume on melting of the amount of solid which fills the lower cylinder, but includes also the thermal expansion of the gas on passing from the temperature of the lower to that of the upper cylinder. Because of the large temperature ranges, this correction is considerable. The full details by which the correction was determined need not be described here. The general method, as already indicated, was to describe isotherms at various temperatures over the range of pressures involved, the difference of the isotherms giving almost directly the thermal expansions necessary. These isotherms were checked after a cycle of pressure and temperature changes by returning to the initial point. This check was almost always highly satisfactory, there being no evidence of leak, or of penetration of the gas into the steel, or permanent deformation of the cylinder. Only once was there a slight and temporary leak at the highest pressure; the character of the plot made so obvious the exact place where this had occurred that small corrections could be easily applied to it, so that it was not necessary to discard the run.

The parameters of the gaseous phase as such were determined only in so far as they were necessary to characterize completely the transition data, but nevertheless a considerable amount of information was thus incidentally obtained of the p - v - t surface in regions not previously explored. This data is tabulated in the following, not at regular temperature intervals, which would have involved interpolations and extrapolations which would perhaps not have been justified, but very nearly in the form in which it was obtained. I hope that at some time in the future this same apparatus may be used to give more systematic information about the p - v - t surface in this region.

DETAILED PRESENTATION OF DATA.

Nitrogen. The nitrogen was obtained from a cylinder of 99.90% purity. I am indebted for this to the special courtesy of the Research Department of the Air Reduction Company. The labels as commercially supplied indicating the purity of nitrogen are highly misleading.

Thus the true meaning of a label "99.90% pure" on a commercial tank is that the oxygen content has been tested and found to be 0.10%. In addition to oxygen, there is of course a considerable impurity of argon in nitrogen obtained from atmospheric sources as is this, and this impurity is not at all indicated by the label. However, my cylinder was specially provided, and I have the statement of the Research Department that the actual nitrogen content of my sample was 99.90%. As always in making these transition determinations, the data themselves give internal evidence, by the sharpness of the transition, of the degree of purity, and the transitions were in fact in the final series of runs always gratifyingly sharp. In some of the early runs, however, sharp transitions were not always obtained, when various difficulties were encountered in sufficiently flushing out the atmospheric air originally filling the apparatus. Not only were the corners sometimes rounded under these conditions, but after freezing had once taken place the impurities sometimes segregated, and did not immediately remix, by diffusion, when melting took place, so that there was the appearance of a discontinuity in the gaseous phase, due to the melting of the segregated impurity, superposed on the main transition. One might in this erroneous way receive the

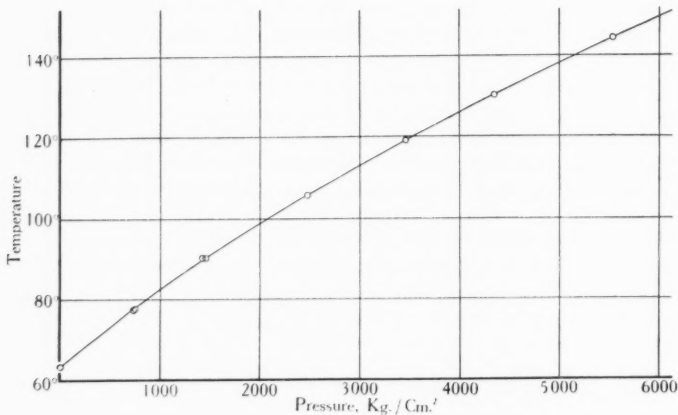


FIGURE 3. The melting temperature of nitrogen in degrees Absolute as a function of pressure.

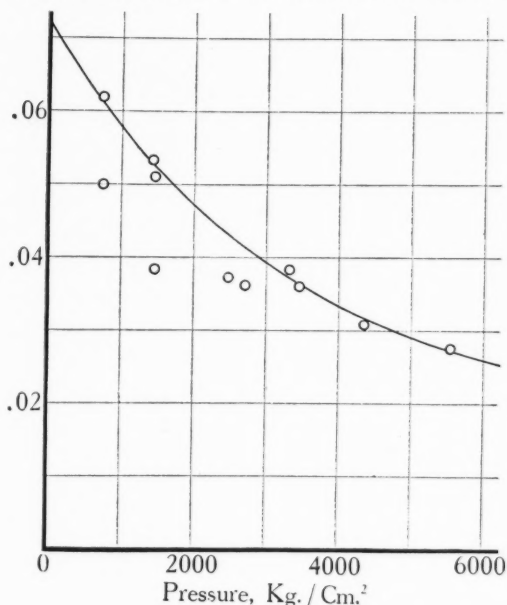


FIGURE 4. The change of volume of nitrogen on melting, in cm^3 per gm, as a function of pressure.

impression that there were degradation phenomena in the gaseous phase at high pressure and low temperature.

In all, runs were made with ten different fillings of the apparatus, of which a few were completely discarded because of either insufficient purity, as shown by the rounding of the corners of the transition, or because of imperfections in various parts of the apparatus, such as the temperature measurements or measurements of piston displacement, before the final details of the apparatus had been worked out. There were about six fillings which gave satisfactory results, either for the transition data or for the various isotherms. The experimental points for the pressure-temperature coordinates of the melting curve are shown in Figure 3, and the changes of volume in Figure 4. The p - t points are sufficiently regular, but one could wish that some of the Δv points had been better. This doubtless means that, in spite of the

precautions, the lower cylinder was not always completely filled with the solid phase. There are probably two reasons for this. In the first place, solid nitrogen seems to have considerable mechanical strength, so that, if the connecting pipe is once plugged with the solid, considerable excess pressure is necessary to force the plug through and build up the proper pressure in the lower cylinder. On several occasions, when the manipulations of lowering the cylinder back into the bath and simultaneously building up the pressure were not made with great care, very nearly steady conditions were attained at pressures several hundred kilograms beyond the transition pressure at a piston displacement corresponding to only partial completion of the transition. That is, the pipe was plugged, and the plug was yielding with extreme slowness because of its mechanical strength. The second reason is probably connected with the fact that nitrogen apparently does not subcool under the conditions of the experiment, for freezing was always observed to start when pressure exceeded the transition pressure by the smallest observable amount. Since the pressure increases are transmitted through the pipe, a nucleus of solid may well have started to form in the pipe before freezing started in the cylinder itself, so that the formation of a plug is especially easy. One must not from this draw the conclusion that nitrogen will not subcool under any conditions; it is quite consistent with my previous experience that it might subcool when contained in a glass vessel, for instance, although it may not subcool in contact with steel.

The most probable errors in Δv appear to be in the direction of too small values, so that in Figure 4 the low lying points were entirely disregarded in drawing the curve.

In Table I are shown the transition data, taken from the data of figures 3 and 4, smoothed and tabulated at intervals of 1000 kg/cm². The freezing point at atmospheric pressure was obtained from International Critical Tables. Table I also contains values of $\frac{d\tau}{dp}$, obtained from a plot of the first differences of temperature against pressure, and finally the latent heat of the transition, L , calculated by Clapeyron's equation, $\frac{d\tau}{dp} = \frac{\tau\Delta v}{L}$, from the other data of the table. The last significant figure in the latent heat is obviously in great doubt.

A most important point to be settled with regard to the melting curve and the data of Table I is whether the melting parameters determined by these experiments refer to α -nitrogen, (low temperature

TABLE I.
MELTING PARAMETERS OF NITROGEN.

Pressure kg/cm ²	Temp. Abs.	$\frac{d\tau}{dp}$	ΔV cm ³ /gm	Latent Heat kg cm/gm
1	63°.2	.0209	.072	218
1000	82 .3	.0176	.058	271
2000	98 .6	.0153	.047	302
3000	113 .0	.0135	.040	334
4000	125 .8	.0124	.033	335
5000	137 .8	.0117	.029	342
6000	149 .2	.0112	.026	346

modification at atmospheric pressure) or to β -nitrogen (high temperature modification). At atmospheric pressure the transition temperature between the two modifications is 35.5° K. The melting curve which is measured at low pressures, as for example in the recent work of Keesom and Lisman up to 110 kg/cm², is obviously that of the β modification. If the high pressure coordinates given above are for the α modification, then there must be a triple point on the melting curve, with discontinuity in direction. The lowest pressure of my measurements was 750 kg; it seems that the assumption of a triple point above this pressure is not consistent with the experimental accuracy. If there is a triple point, therefore, it must be between 110 and 750 kg. In this range there are only the measurements of Simon, but when these are plotted on a large scale it appears that there is too much irregularity to settle the point. The argument must therefore be more or less indirect. If the thermodynamic parameters for the transition from α to β were accurately known, the slope of the transition line could be computed and the question settled. This unfortunately is not the case; the latent heat of the transition is accurately known from the work of Giauque and Clayton,⁵ but the values for the volume of the two solid modifications are very conflicting. Thus Dewar⁶ gives for the density of the solid at 63° K 0.879 gm/cm³, Simon finds 0.95₆, and Keesom and Lisman find 0.947 by calculation from their own $\frac{d\tau}{dp}$ and the latent heat of Giauque. There are X-ray measurements of the density of β -nitrogen: 0.995 at 39° K by Ruhemann⁷ and 0.982 at 45° by Vegard.⁸ The crystal structure of α -nitrogen has been determined at liquid hydrogen temperature by de

Smedt, Keesom and Mooy,⁹ who find that the structure is probably tetragonal with four atoms in the cell and density of 1.03. It would seem probable therefore that the density of α -nitrogen is greater than that of β -nitrogen at the transition point, which means that the transition line rises, and that therefore a triple point on the melting line is a possibility. Further indirect evidence is contained in the data of Keesom and Lisman for the melting parameters up to 110 kg.

Their initial slope is $\frac{d\tau}{dp} = 0.0222$ against 0.0209, my extrapolated

value by drawing a smooth curve with no triple point, and their Δv at atmospheric pressure, 0.092, is much higher than my 0.072, obtained by smooth extrapolation. These discrepancies are evidence of something the matter, but the disturbing feature is that the discrepancies at first appear to be in the wrong direction to be accounted for by a triple point, since my latent heat should be the sum of the melting heat of β and the transition heat and therefore larger than the heat of Giauque, and my Δv should be the sum of the Δv of liquid $-\beta$ and $\alpha-\beta$ and therefore larger than the value of Keesom and Lisman, instead of smaller. It appears to me that the solution may be found in a very rapid variation of the properties of β -nitrogen in its domain

of stable existence. That is, the slope $\frac{d\tau}{dp}$ must drop rapidly along the melting curve, and its Δv must also fall rapidly. As far as the slope of the melting curve goes this is consistent with the data of Keesom and Lisman, for the formula by which they reproduce their results has initially a slope 6% greater than mine, which means that initially their temperatures lie above my smooth curve, but at 2000 kg their formula gives a melting temperature 6.7° lower than mine. A bit of confirmatory evidence is that at low pressures the temperatures of Simon are a trifle higher than mine, whereas at high pressures they become rapidly lower. It seems, therefore, probable to me that there is a triple point below 750 kg, that there is rapid variation in the properties of β -nitrogen, and that the parameters of the melting curve given in Table I are for the melting of the α modification. This solution cannot be regarded as entirely satisfactory, however, and must wait for final confirmation for accurate measurements of the melting parameters in the pressure range below 750 kg, and for a good determination of the difference of density of the α and β modifications at the atmospheric transition point.

TABLE II.
VOLUME OF 1 GM OF NITROGEN.

Pressure kg/cm ²	Volume, cm ³				
	+23°.5 C	0°	-50°	-100°	-140°
3000	1.2374	1.2069	1.1422	1.0754	1.0226
4000	1.1615	1.1391	1.0881	1.0327	.9876
5000	1.1061	1.0870	1.0451	.9997	.9613
6000	1.0652	1.0487	1.0117	.9729	.9412

In Table II are given the volumes of the gas at regular pressure and temperature intervals. This table is based on my previous values for the volume at pressures above 3000 kg/cm² at 68° C, reducing these values to other temperatures by means of the thermal expansions determined in this investigation. My previous work, in turn, was based on the fiducial volume of Amagat¹⁰ at 3000 and 68°. Amagat also determined the thermal expansion at 3000 kg. His value for the mean expansion between 0° and 68° at 3000 kg differs by 2% of itself from the value found by me in the present investigation. The volumes of the gas given in Table II are not sufficient for all the reductions necessary in computing the parameters of Table I, since they do not extend below 2000 kg. Additional information needed at the lower pressures was as follows: at the freezing point at boiling nitrogen temperature, that is, at 745 kg/cm² and 77.5° K, one gram of gas occupies 1.138 cm³. At the boiling oxygen freezing point, that is, at 1472 kg/cm² and 90.25° K one gram of gas occupies 1.123 cm³.

Table II gives the means for finding the volume of the gas at various points of the freezing line; there were direct experimental values at three higher pressures as well as at the points just mentioned. The following appear to be the best values for the volume of one gram of the gaseous (amorphous) phase at pressures on the melting curve of 1, 1000, 2000, 3000, 4000, 5000, and 6000 kg/cm² respectively: 1.140, 1.137, 1.094, 1.010, 0.980, 0.962, and 0.956. The sudden drop and point of inflection between 1500 and 3500 is unexpected, but the curve as given passes exactly, to the last significant figure, through my five experimental points and the point at atmospheric pressure determined by Baly and Donnan as quoted in Smithsonian Tables. An additional experimental point at 2500 to clinch matters would

have been desirable, but unfortunately two attempts to put a point here were frustrated by leaks. The curve for the volume of the solid phase along the melting line may be found at once from the data just given and from the data of Table I, the shape of the curve is very much like that for the shape of the amorphous phase, except that the variations are not so pronounced.

Argon. The argon was obtained from the Cleveland Lamp Division of the General Electric Company, to whom I am much indebted. It was purified by a process recently developed for use in directly filling lamps without further purification. The impurity is stated to be only 0.1%. I used it without further purification; the transitions were sharp, indicating sufficient purity.

The measurements on argon were made after the apparatus had been perfected and after experience with the manipulations had been gained by the work on nitrogen, so that not so many runs were necessary; six fillings in all were made of the high pressure apparatus, and in addition several fillings of the bottle in order to get a fiducial point on the p - v - t surface.

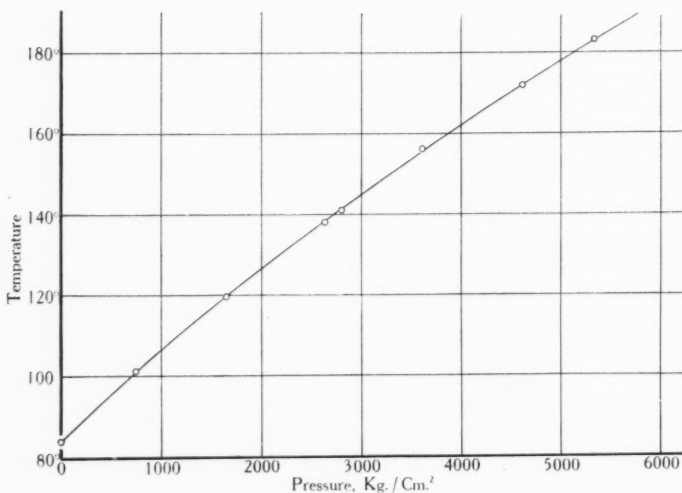


FIGURE 5. The melting temperature of argon in degrees Absolute as a function of pressure.

The experimental p - t points on the melting curve are shown in Figure 5 and the experimental values of Δv in Figure 6. It will be

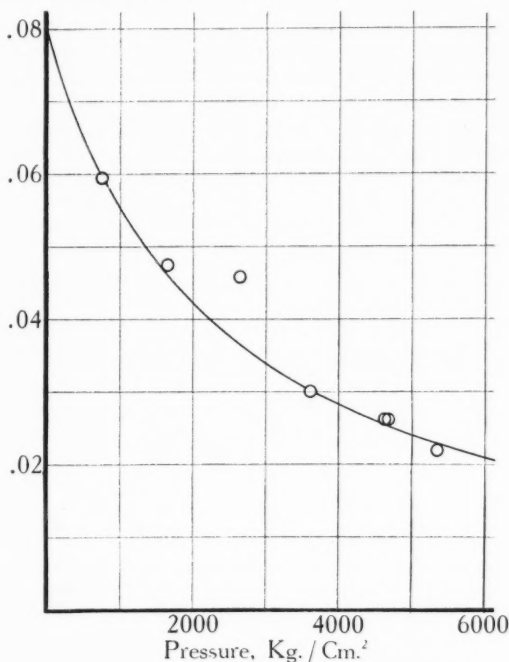


FIGURE 6. The change of volume of argon on melting, in cm^3 per gm, as a function of pressure.

seen that in general the Δv points lie much more smoothly than for nitrogen. Neither of the reasons suggested for the irregular results of nitrogen seem to be operative in the case of argon. In the first place, argon was several times observed to subcool, excess pressures of 100 kg or more being possible before freezing takes place. As already suggested, this characteristic would tend to result in the formation of the first nucleus of the solid in the cylinder itself rather than in the connecting pipe, with less likelihood of a plug of solid in the pipe.

In the second place, the mechanical strength of solid argon is apparently not as high as that of solid nitrogen, and no phenomena were observed with argon which would suggest the plugging of the pipe. In fact, on one occasion the change of volume on freezing was measured without taking any of the regular precautions to ensure freezing from the bottom of the lower cylinder, and the point thus obtained lay smoothly on the curve with the others.

The melting parameters, at regular intervals and smoothed, are given in Table III; the melting point at atmospheric pressure was taken from International Critical Tables.

TABLE III.
MELTING PARAMETERS OF ARGON.

Pressure kg/cm ²	Temp. Abs.	$\frac{dz}{dp}$	ΔV cm ³ /gm	Latent Heat kg cm/gm
1	83°.9	.0238	.0795	280
1000	106 .4	.0211	.0555	280
2000	126 .3	.0192	.0425	279
3000	144 .9	.0178	.0340	277
4000	161 .9	.0165	.0280	275
5000	177 .8	.0155	.0240	276
6000	192 .9	.0146	.0210	277

The volumes of the amorphous phase, at regular pressure intervals and various odd temperatures determined by the accidents of the thermostat settings for the transition measurements, are given in Table IV. The values at 55° C are taken over directly from previous work, it now being possible to give the absolute volumes instead of only the volume changes, which alone was possible previously.

Table IV provides the means by which the volume of the amorphous phase may be found at various points on the melting curve. There are also approximate experimental values for these same quantities; the experimental point at 750 kg/cm² lies too high to fit in with the other points and the known value at atmospheric pressure; the experimental points at higher pressures lie fairly well on a smooth curve. The following seem to be the best values for the volume in cm³ of 1 gm of the amorphous phase at various points on the melting curve: 1 kg, 0.702 cm³; 2000 kg, 0.656 cm³; 4000 kg, 0.638 cm³; 6000 kg, 0.628 cm³. The corresponding values for the volume of the solid are: 0.622,

TABLE IV.
VOLUME OF 1 GM OF ARGON.

Pressure kg/cm ²	Volume, cm ³							
	+55° C	+25°	0°	-90°.0	-101°.4	-117°	-135°.1	-153°.5
700		1.262	1.179					
800		1.175	1.105					.690
900		1.110	1.048					
1000		1.060	1.006					.697
1100		1.020	.970					
1200		.989	.943					
1300		.962	.920					.677
1400		.938	.899					
1500		.916	.880					
1600		.898	.864					.657
1700		.883	.852					
1800		.870	.840					
1900		.857	.828					
2000	.880	.846	.818					
2500	.831	.808	.785		.687		.653	
3000	.797	.773	.753	.671	.667			
3500	.772	.751	.733	.661	.656	.638		
4000	.748	.729	.713	.650	.642			
4500	.730	.712	.697	.641	.632			
5000	.712	.695	.681	.631				
5500	.698	.682	.669	.624				
6000	.685							
7000	.663							
8000	.645							
9000	.630							
10000	.617							
11000	.607							
12000	.596							
13000	.588							
14000	.580							
15000	.573							

0.613, 0.610, and 0.607. This approximate constancy may be of some theoretical significance.

DISCUSSION.

A comparison of my p - t - v values of the gas with those of other observers is not possible, for there are no other determinations in this range; the only other values for the freezing parameters are those of Simon and collaborators for the p - t coordinates. Simon's melting curves for both nitrogen and argon run mostly below mine, that is, at a given pressure his melting temperature is lower than mine. For

argon the discrepancy increases from 0 at atmospheric pressure to a maximum of about 2.5° at 1400 kg, between 1400 and 3400 the discrepancy is roughly constant, becoming less, if anything, at the higher pressures. For nitrogen the discrepancy is more serious. Up to 1400 his curve lies slightly higher than mine, by not more than 0.2° or 0.3° , but at 1400 it crosses, and from here on the divergence increases rapidly with increasing pressure, becoming more than 6° at 4900. The discrepancy is in the direction that would indicate impurity in Simon's material, but I believe that this is not the explanation and that the reason for the discrepancy can be found in Simon's method. This was the method of the stopping of a capillary tubing first used by Keesom¹¹ in finding the freezing curve of helium. A capillary tube filled with the gas connects at either end with a pressure gauge, the central part of the capillary being maintained at the temperature at which the freezing pressure is to be determined. Pressure is increased by pushing a plunger into a cylinder connected to one end of the capillary, resulting in a rise of pressure in both gauges as long as the substance remains fluid, but when the substance freezes the capillary is plugged and only the one gauge responds to a further decrease of volume. A source of error in the method, apparently not discussed either by Keesom or Simon, is the fact that the plug of solid in the capillary must be under a shearing stress, and it is known by thermodynamics that the freezing temperature is always depressed by a shearing stress by an amount proportional to the square of the stress and to the absolute temperature. The fact that the discrepancies are markedly greater with nitrogen than with argon fits in perfectly with the observation made above that the pipe plugs much more easily with nitrogen than argon, involving a greater mechanical strength in the solid nitrogen and consequent greater shearing stress in it. The rapid increase of the discrepancy in nitrogen at high pressures is also consistent with this suggestion; the discrepancy would increase because of the increased viscosity or shearing strength to be expected in solid nitrogen in virtue of the increasing pressure, and it would also increase because of the absolute temperature factor in the thermodynamic formula. On the other hand, there would be a decreasing tendency because of the decreased strength to be expected at higher temperatures; in view of other experience at high pressures I would expect the first tendency much to preponderate. It would be an easy matter to find whether this is actually an important source of error if experiments by the method of Keesom are repeated in the future;

if the effect is unimportant, the freezing pressure should be independent of the diameter of the capillary, whereas if the effect is important, the apparent freezing temperature should increase as the diameter of the capillary increases. Apparently the size of the capillary was not varied in previous experiments; the diameter of Simon's capillary was only 0.15 mm.

The fundamental question raised by this investigation with regard to the existence of a critical point, crystalline-amorphous, must already have been answered by the reader from an inspection of Tables I and III. If there is a critical point, the curves of latent heats and volume differences must be such that they will extrapolate to a common vanishing point. For argon the latent heat is almost exactly constant, whereas for nitrogen it increases, comparatively rapidly at first (which may be an effect of the disregarded triple point), but it also is approximately constant between 3000 and 6000 kg/cm². The volume differences on the other hand decrease, but the curve is convex toward the pressure axis in such a way as not to indicate vanishing at any finite pressure. Furthermore, if the changes of volume and the slope of the melting curve, $\frac{d\tau}{dp}$, are plotted against

temperature instead of pressure, in every case the curve will be found to be convex toward the temperature axis. In all these respects the behavior of nitrogen and argon is not different from that of all other substances whose melting parameters under pressure have been determined, and there is still absolutely no evidence which would lead one to expect the existence of a critical point or to expect that the melting curve does otherwise than rise to indefinitely high pressure and temperature, with a curvature becoming continually less, a difference of volume between the two phases becoming continually smaller, and a latent heat tending on the whole to remain constant or to increase.

In retrospect it is a little difficult to see why a permanent gas should be expected to give any more valuable evidence as to the character of the melting curve than other substances. Simon makes the point that in the case of helium, which unfortunately could not be investigated here, the critical temperature, gas-liquid, has been exceeded in his measurements by a factor of 8, whereas previously the maximum excess was only 20%, in the case of CO₂. But what the precise significance of this is does not appear in the absence of any theory indicating a connection between the phenomena of passage from vapor

to liquid and passage from amorphous to crystalline phase, and in any event it does not appear why it should be more informing to exceed the critical temperature 8 fold than to exceed the critical pressure 165 fold, which had already been done. In fact, the great difference between the relative rôles played by pressure and temperature on the vaporization and the melting curves, as shown by the difference between the factors 8 and 165, should itself indicate a vital difference between the phenomena of vaporization of the liquid and of crystallization of the liquid.

There are a number of minor points which may now profitably be discussed. The latent heats of melting at atmospheric pressure given in Tables I and III, which were obtained by extrapolation from the last experimental point at 750 kg/cm^2 , may be compared with the directly determined values of other observers. For nitrogen my extrapolated value is 218 kg cm/gm against 259 of Giauque. For argon my extrapolated value is 280 kg cm/gm against 287 of International Critical Tables. It may be mentioned that all my computations and extrapolations were made before these previous values were consulted, and that no adjustment was made afterward. The better agreement in the case of argon is, doubtless, to be explained in part by the better values for Δv which it was possible to obtain for argon, and in the case of nitrogen there is the unsettled point of a possible triple point. I do not believe, however, that all the discrepancy can be laid on my Δv values, but I believe that there may be error in the previous values at atmospheric pressure. Simon comments on the well known inaccuracy on the density of the solid phase at atmospheric pressure, a datum which enters the latent heat.

The difference of energy, ΔE , between liquid and solid is of interest as well as the latent heat. The energy difference is obtained by subtracting from the latent heat the mechanical work during melting, or $p\Delta v$. The term $p\Delta v$ is given in Tables I and III. Plotted against pressure or temperature it rises continuously, concave toward the pressure or temperature axis, with continually decreasing curvature. The ΔE curve has much the same character as the Δv curve, falling with increasing pressure or temperature, but convex toward the axis in such a way as not to indicate vanishing at any finite pressure or temperature. The character of the $p\Delta v$ curve also gives some insight into the behavior of Δv itself as a function of pressure. If Δv vanishes at a finite pressure or temperature, the $p\Delta v$ curve must cross the axis at the corresponding point and there is no indication of this.

Furthermore, if Δv vanishes at infinite pressure, and if the $p\Delta v$ curve continues to rise, as it does in the experimental range, then Δv must vanish with infinite pressure less rapidly than it would if the relation between p and Δv were of a simple hyperbolic type.

In setting up a theory of the melting curve and its ultimate course it would seem that some significance should be attached to the volumes of liquid and solid phases along the melting curve. Such information has been available in only a few cases hitherto, there being very few substances whose p - v - t surfaces have been determined for both liquid and solid phases. In the case of water and mercury it was known, however, that volume of both liquid and solid decreases with rising temperature and pressure along the melting curve. We now add to this the information that the volumes of nitrogen and argon also decrease. It would therefore appear not unlikely that this may be the general state of affairs. In fact Simon drops the remark that the volume of the liquid "must" decrease along the melting curve. Such a state of affairs is, doubtless, consistent with our rough general expectations, because as the disorienting effect of temperature increases it would seem natural that the molecules should have to be brought into closer contact to induce crystallization. But this can be only a partial picture, because we know from thermodynamics that freezing is not produced by any condition in the liquid phase alone, but takes place only when there is a proper relation between both phases, a consideration which does not enter the crude picture just presented. I believe that in the absence of any general theory the expectation that the volume of the liquid phase *always* decreases along the melting curve is premature. In fact, the data obtained above suggest that theory might take as a rough first approximation the assumption that the volume of the liquid is constant along the melting line.

Turning now to the new data for the gaseous phase alone, the determination of the volume of argon at one fiducial point makes it possible to compute the p - v values at high pressures using data previously found. The relative p - v values at 0° C and 55° C are given in Table V. In computing these values, the volume of 1 gm of argon at 1 kg/cm² at 0° C was taken to be 580.3 cm³, and the perfect gas law was assumed to hold at atmospheric pressure between 0° and 55°. At high pressures the curve of p - v against pressure is normal, being slightly concave toward the pressure axis. Compared with nitrogen at 68°, hydrogen at 65°, and helium at 55°, the only other gases for which p - v is known at high pressures and which will be found in Figure

TABLE V.

RELATIVE VALUES OF PV FOR ARGON.

Pressure kg/cm ²	PV		Pressure kg/cm ²	PV	
	0°	55°		0°	55°
1	1.000	1.00	8000		7.40
1000	1.733		9000		8.14
2000	2.818	2.52	10000		8.85
3000	3.89	3.43	11000		9.58
4000	4.91	4.29	12000		10.26
5000	5.87	5.10	13000		10.97
6000		5.89	14000		11.65
7000		6.65	15000		12.33

4 of my previous paper,¹² $p\bar{v}$ for argon at 55° is between that of nitrogen and hydrogen, and is roughly twice that of helium. At pressures below 2000 kg/cm², $p\bar{v}$ for argon starts out by being convex toward the pressure axis; this convexity is much more marked at 0° than at 55°, and is of course a result of the fact that at 0° argon is relatively much nearer its critical temperature than the other gases at the temperatures mentioned.

The data contained in Tables II and IV give much better values for the thermal expansion of nitrogen and argon than were obtained in my previous measurements, which were only very rough, and in fact I did not venture to give the values in detail. One check on the values now obtained has already been mentioned, namely that at 3000 kg/cm² my thermal expansion of nitrogen agrees within 2.5% with that of Amagat. At higher pressures there are no previous values for comparison. It is seen that thermal expansion regularly decreases with increasing pressure and is less by a factor of several fold than it would be for a perfect gas. In fact it is smaller than for many liquids, such as alcohol, under normal conditions. Thus for nitrogen the thermal expansion at 0° C at 3000 kg/cm² is less by a factor of 3.4 than for a perfect gas, and at 6000 is less by a factor of about 5.5. Similarly, the thermal expansion of argon at 0° at 2000 is less by a factor of 2.82 than for a perfect gas, and at 5000 is less by a factor of 5.9. $p\bar{v}$, on the other hand, differs more from the perfect gas values for nitrogen than for argon. This means that the compressibility of nitrogen differs more from the perfect gas value than does that

of argon, but its thermal expansion differs less. The relatively high thermal expansion of nitrogen, as compared with that of argon, tends to become more marked when extrapolated to higher pressures. It is known that a small thermal expansion means a law of force between the molecules which is nearly linear, exact linearity leading to zero thermal expansion, so that the forces in nitrogen at high pressures are not so nearly linear as in argon. This might be expected of a diatomic substance as compared with a monatomic one.

It is of interest to find the change of internal energy with pressure along an isothermal of the two gases at high pressures. This is given by the formula $\left(\frac{\partial E}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\tau$. $\left(\frac{\partial E}{\partial p}\right)_\tau$ is zero for a perfect gas, but for condensed phases is initially negative, and changes sign at some high pressure. The pressure of the change of sign is the pressure at which the attractive and repulsive forces are in balance. A rough calculation shows that in the case of nitrogen the pressure of reversal is between 4000 and 5000 kg/cm² at room temperature, and between 5000 and 6000 at -120° C. The volume at the reversal point is markedly higher at the higher temperature. The minimum of E is very flat however, and its exact location is therefore subject to experimental error, so that possibly the variation just stated in the pressure of reversal with temperature is not significant. For argon, on the other hand, the reversal has not yet been reached in the range covered in Table IV. It is also known that the reversal point of helium must occur at pressures probably above 15000 kg/cm² at 55°; this suggests a possible essential difference between diatomic and monatomic substances.

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